

## Relation between various chromium compounds and some other elements in fumes from manual metal arc stainless steel welding

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### Abstract

For the years 1987-1990 160 individual samples of manual metal arc stainless steel (**MMA/SS**) welding fumes from the breathing zone of welders in four industrial plants were collected. Concentrations of soluble and insoluble chromium (Cr) III and Cr VI compounds as well as of some other welding fume elements (Fe, Mn, Ni, F) were determined. Concentration of welding fumes in the breathing zone ranged from 0.2 to 23.4 mg/m<sup>3</sup>. Total Cr amounted to 0.005-0.991 mg/m<sup>3</sup> (including 0.005-0.842 mg/m<sup>3</sup> Cr VI). Total Cr content of fumes varied from 0.1 to 7.4%. The distribution of particular Cr compounds was: 52.6% soluble Cr (including 50.7% Cr VI), 65.5% total Cr VI, and 11.4% insoluble Cr VI. The results obtained indicate that **MMA/SS** welding is a process that could be highly hazardous to human health. Evaluation of occupational exposure has shown that **MMA/SS** welders may exceed the admissible concentrations of soluble and insoluble Cr VI forms as well as of **Mn** and **Ni**. In the plants investigated the sum of the ratios of concentrations of particular welding fumes in the breathing zone of welders exceeded corresponding maximum allowable concentration values by 24 times (including 17 times for total Cr VI). Due to the variety and changeability of particular parameters occurring in the working environment, the composition of **MMA/SS** welding fumes (in the welder's breathing zone) is so variable that it is not possible to assess the exposure by means of

one universal exposure indicator (maximum additive hygienic limit value). The evaluation should be based on the results of measurements of concentrations of particular elements in welding fumes.

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Occupational exposure to chromium (Cr) poses a serious problem and many studies on the biological effects of chromates have been conducted.<sup>1-3</sup> Chromates are well recognised as human carcinogens and suspected of genotoxic action.<sup>4,5</sup>

Numerous epidemiological studies have been carried out to determine the relation between human exposure to chromates and the occurrence of lung cancer, but only some of them include measurements of exposure in stainless steel (SS) welders.<sup>6</sup> The level of exposure of workers to metal fumes, fluxes, and gases depends, to a large extent, on the type of welding.<sup>7</sup> Welding techniques vary, although most stainless steel welding is performed with electric arc (manual metal arc (**MMA**)) processes.

The chemical composition of **MMA/SS** welding fumes and details of occupational exposure of welders in the workplace have been reviewed.<sup>8</sup> Particular attention has been paid to Cr oxidation state in welding fumes.<sup>9</sup>

A few studies devoted to occupational exposure of **MMA/SS** welders have considered Cr compounds of different solubilities and at different oxidation states.<sup>10</sup> In our previous studies, the analytical procedure for simultaneous determination of soluble and insoluble Cr III and Cr VI as well as of some other elements in welding fumes was presented for evaluation of occupational exposure of welders.<sup>11-15</sup>

This study was aimed at evaluation of welders' occupational exposure to Cr III and Cr VI compounds, as well as to some other elements in **MMA/SS** welding fumes, in selected Polish industries.

### Materials and methods

#### SUBJECTS AND EXPOSURE

The study covered the workers at a plant where some

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Table 1 Composition of welding materials

Plants	Stainless steel	Electrode type	Content	
			Cr (%)	Ni (%)
A	1H18 N9T	ES 18-8 SiBB ES 18-8 2B	18	8
B	08H18 N10T	EA 400/10T EA 395/9 AVESTA P-5	17-19 13.5-17 22	9-12 22-25 12-14
C	0H 17 T	ES 20-1-6B	18	8
D	H 18 N9T	ES 188B MVRAC/DC(AR)	18 19.5	8 10

items of equipment for power stations were manufactured (A), a chemical industry plant (B), and two metal industry plants (C, D). All plants were equipped with dilution ventilation with blowing and exhaust systems. Local exhaust systems were used only at the welding sites in plant C. Table 1 presents the materials used in the welding process in particular plants.

#### PROCEDURE

Throughout 1988-90 about 120 individual samples of MMA/SS welding fumes in the breathing zone of welders and 40 individual samples from welder assistants in the four industrial plants (A, B, C, D) were collected. During the regular eight hour shift the welders were occupied either with welding or with assembly work connected with the welding process for about six and a half to seven hours. Two air samples a shift were collected simultaneously in a welder's breathing zone (behind the face guard), each over a period of about seven hours. Two stage personal air sampling was applied (Casella AFC-123, flow rate 1.9 l/min). The respirable fraction of dust was collected on a membrane filter (Sartorius 11304, 0.8 µm, Ø37 mm) and a glass fibre filter (Whatman GF/A, 0.37 mm). Methods of sample collection, preparation, and analytical procedures have been presented earlier.<sup>12</sup>

Before and after sampling filters were dried at 105°C for one hour, then cooled in a desiccator and weighed. Next the mass of dry substance was calculated by comparing filter mass before and after the sampling.

#### Membrane filter

In one part of the sample from the membrane filter Fe, Mn, Ni, and Cr were determined by atomic absorption spectroscopy. In the other part of the membrane filter sample, fluorides were determined after microdiffusion using a colorimetric method with a zirconium-SPANDS complex.

#### Glass fibre filter

In one part of the glass filter total soluble Cr was determined by atomic absorption spectroscopy after water extraction. Soluble Cr III was separated from soluble Cr VI in a column filled with s-diphenylcarbazide resin, which retains Cr VI. Soluble Cr III was determined in the eluate. After alkaline extraction of the sample, insoluble Cr VI was determined in the insoluble residue by a colorimetric method with s-

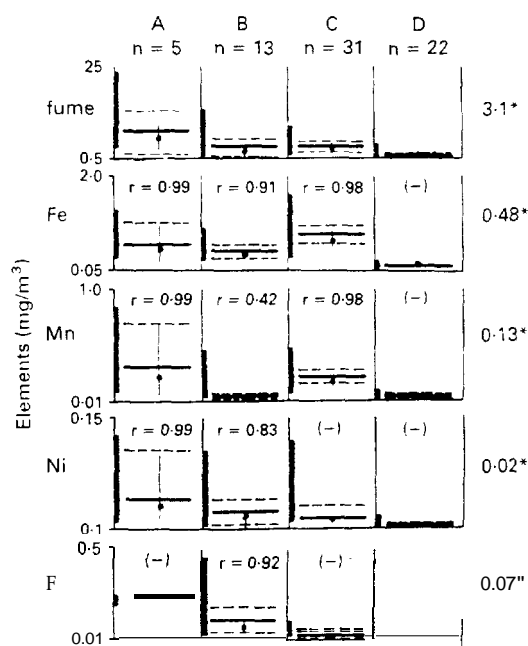


Figure 1 TWA (8 h) concentrations of elements in MMA/SS welding fumes ( $\text{mg}/\text{m}^3$ ). TWA = time weighted average; A, B, C, D = plants; I = range of concentrations; — = arithmetic mean (with confidence intervals);

● = geometric mean (with confidence intervals);  
\* = mean values of concentrations in all tested plants;  
r = correlation coefficient; n = number of measurements;  
(-) = no correlation ( $p > 0.05$ ).

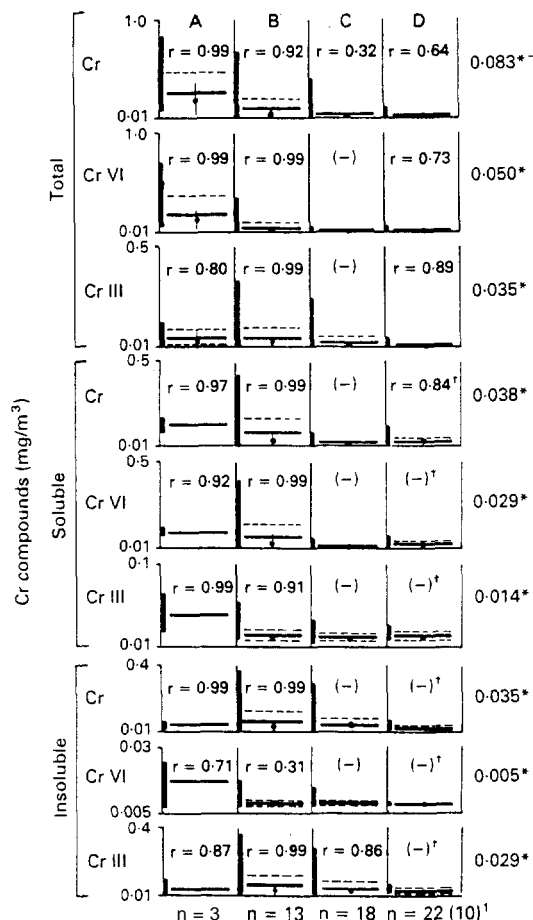


Figure 2 TWA (8h) concentrations of particular Cr compounds in MMA/SS welding fumes ( $\text{mg}/\text{m}^3$ ) (explanations as in fig 1).

diphenylcarbazine. The second part of the glass filter was used to assess the content of total Cr VI by the same method. All other Cr values were calculated by difference.

## Results

Figures 1 and 2 present the time weighted average concentrations (TWA-8h) of welding fumes and their major elements (Fe, Mn, Ni, F, Cr) as well as of particular Cr forms (soluble and insoluble Cr III and Cr VI) in the air ( $\text{mg}/\text{m}^3$ ) of the particular industrial plants (A, B, C, D). They also show mean concentration values from all plants. Welding fume concentrations in the welders' breathing zone ranged from 0.2 to  $23.4 \text{ mg}/\text{m}^3$ . The maximum concentration was found in plant A (mean  $9.0 \text{ mg}/\text{m}^3$ ; range 2.8–23.4

$\text{mg}/\text{m}^3$ ). In plant C, considerably higher concentrations of fumes were found in the welders' breathing zone (mean  $3.5 \text{ mg}/\text{m}^3$ ; range 1.0–9.1  $\text{mg}/\text{m}^3$ ) than in that of the welders' assistants (mean  $0.8 \text{ mg}/\text{m}^3$ ; range 0.2–1.9  $\text{mg}/\text{m}^3$ ) who only occasionally stayed at the welding posts. Mean fume concentrations in plants B and D amounted to  $3.2 \text{ mg}/\text{m}^3$  and  $1.3 \text{ mg}/\text{m}^3$  respectively.

Similar values of respirable dust fraction concentrations were obtained in the samples collected in the breathing zone of welders simultaneously on a membrane filter and a glass fibre filter ( $r = 0.75\text{--}0.98$ ).

Mean weighted total Cr concentration in the breathing zone of welders ranged from 0.005 to  $0.991 \text{ mg}/\text{m}^3$  (fig 2). The highest total Cr concentration was found in plants A and B in which the work was performed in a half closed area without local exhausts and in a forced body position.

Figure 3 presents the content of particular elements of fumes. The data indicate that the chemical content of fumes in the breathing zone of welders varied greatly. Total Cr in the fumes occurring in the breathing zone of all welders ranged from 0.1% to 7.4%. Mean values of total Cr (Y<sub>0</sub>) in plants A, B, C, and D were 3.4%, 2.5%, 1.4%, and 2.6% respectively.

The relations between concentrations of particular constituents—namely, Fe, Mn, Ni, and Cr—and concentration of fumes are presented in the form of correlation coefficients and regressions of the type  $y = a + bx$  in particular plants (fig 1) and graphically in the form of simplified lines of the type  $y = kx \pm k$  for all plants (fig 4). A low correlation coefficient and lack of linear dependence were obtained for total Cr in plant C (welders and their assistants together; fig 2). Figure 4 presents graphically the relation between concentrations obtained for all plants (disregarding welders' assistants from plant C). Total Cr concentration with regard to fumes was characterised by a high correlation coefficient ( $r = 0.89$ ).

The results obtained from regression lines ( $n = 59$ ,  $p = 0.05$ ) have facilitated calculation of the mean content of particular elements in fumes (table 2).

Similar relations were determined for concentrations of particular Cr forms with regard to fume concentration in all plants tested. Figure 5 presents these graphically. Table 3 shows the mean content (%) of particular Cr forms in the fumes. This was determined from regression lines  $y = kx \pm k$ . Participation of particular Cr forms in relation to total Cr was determined in the same way (fig 6, table 4). The relations presented indicate that participation of particular Cr forms compared with total Cr content in all samples determined (samples exceeding the sensitivity of the method) was similar (table 4).

Due to considerable variability in the content of fumes in the MMA/SS welders' breathing zone, the evaluation of exposure was based on TWA (8 h)

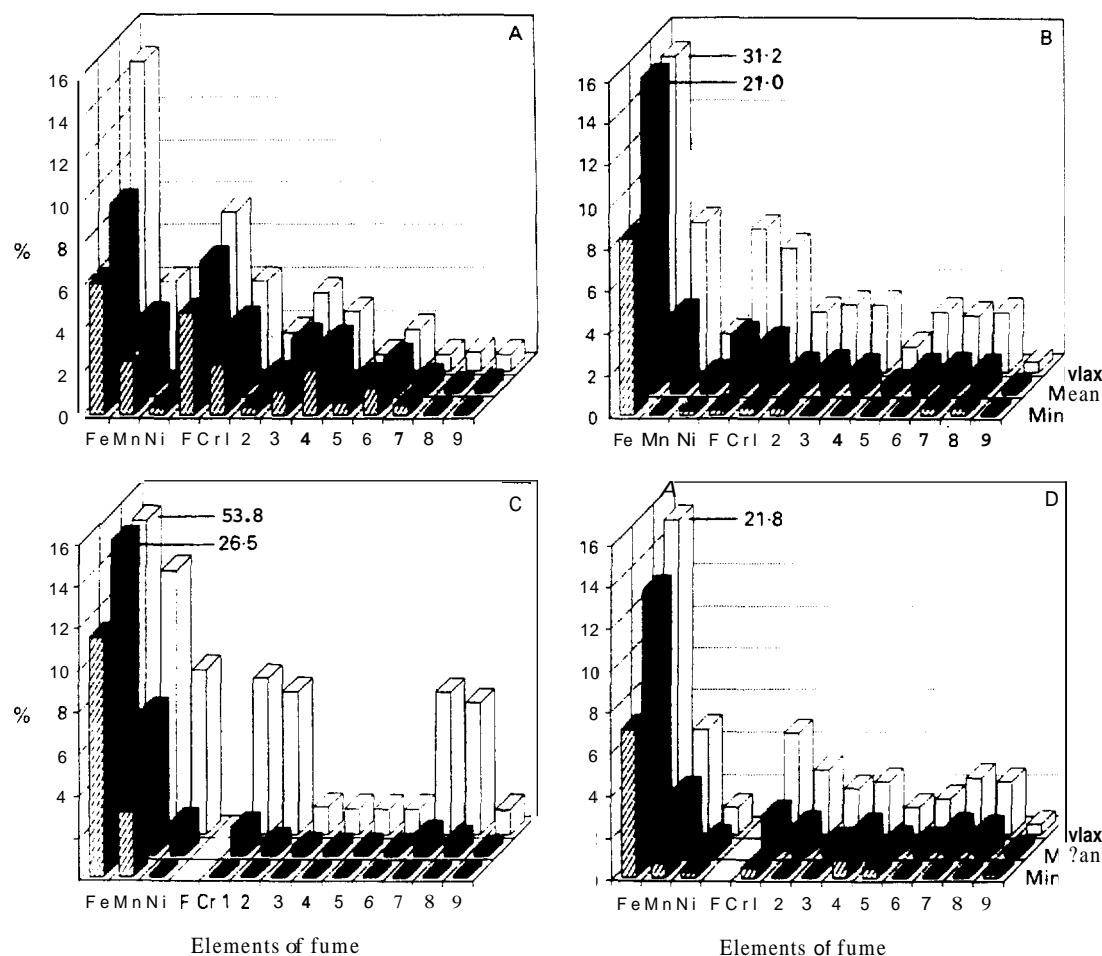


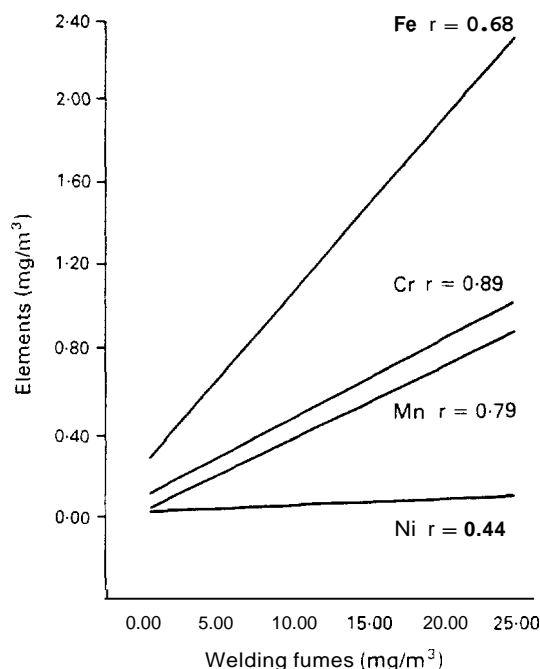
Figure 3 Percentage content of elements and particular Cr compounds in tested plants (A, B, C, D). Cr 1 = total Cr; 2 = soluble Cr; 3 = soluble Cr III; 4 = soluble Cr VI; 5 = total Cr VI; 6 = insoluble Cr; 7 = insoluble Cr III; 8 = insoluble Cr VI; 9 = total Cr III.

concentrations of fumes for particular elements (Fe, Mn, Ni, F, Cr VI, Cr III) adopting the principle of their cumulative toxic effect. The evaluation of combined occupational exposure (figs 7-9) allowed us to ascertain that maximum allowable concentrations (MAC) values were exceeded in 42.5% of MMA/SS welders ( $n=72$ ). Individual welders' combined exposure to the elements in fumes was 24 times the admissible value for Cr VI, 17 times for Ni and three times for Mn in plant A (fig 7). The hygienic standards for various Cr forms, mandatory in some other countries, were exceeded for total Cr VI and soluble Cr VI in 23-25% of results and for soluble Cr VI in 5% of results, whereas no form of Cr III exceeded hygienic standards (table 5).

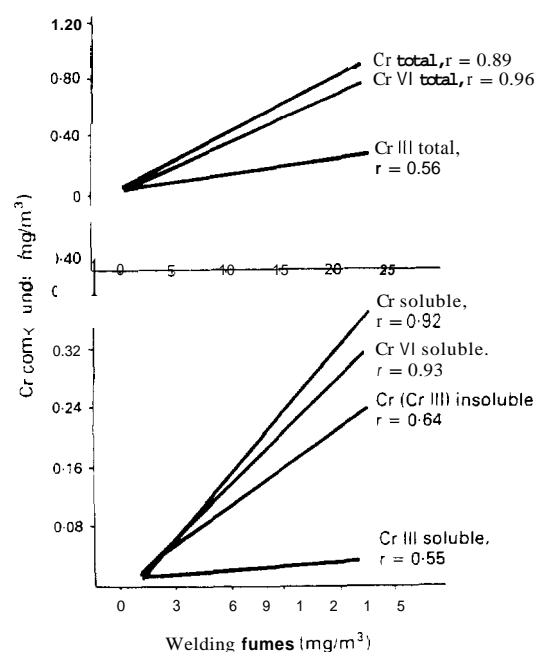
## Discussion

The concentration of MMAiSS welding fumes may vary in particular workplaces from a few to several hundred  $\text{mg}/\text{m}^3$ .<sup>28</sup> Stern,<sup>21</sup> generalised the data for Swedish and Danish workplaces and found that for MMA/SS processes the medium TWA (8 h) total dust concentration in the breathing zone varied from 1.5 to 10  $\text{mg}/\text{m}^3$ . An indicator of the range of exposures to total particles was provided by Ulfvarson.<sup>16</sup>

Our studies, performed in detail for the first time in Polish industry, indicated that the TWA (8 h) of respirable fraction of MMA/SS fumes in the welders breathing zone ranged from 0.2 to 23.4  $\text{mg}/\text{m}^3$  (mean 3.1  $\text{mg}/\text{m}^3$ ) (fig 1).



**Figure 4** Relation between TWA (8 h) concentrations of elements and MMA/SS welding fumes (plants A, B, C, D). Number of measurements performed; =60.  $y = \text{correlation line } y = kx \pm k$  for: Fe  $0.112x \pm 0.21$ ; Mn  $0.039x \pm 0.006$ ; Ni  $0.005x \pm 0.002$ ; Cr  $0.036x \pm 0.005$ .



**Figure 5** Relation between TWA (8 h) concentrations of particular Cr compounds and MMA/SS welding fumes (plants A, B, C, D).  $y = \text{correlation line } y = kx \pm k$  for: total Cr  $0.036x \pm 0.005$ ; total Cr VI  $0.025x \pm 0.003$ ; total Cr III  $0.011x \pm 0.003$ ; soluble Cr  $0.023x \pm 0.004$ ; soluble Cr VI  $0.023x \pm 0.004$ ; soluble Cr III  $0.004x \pm 0.001$ ; insoluble Cr III  $0.016x \pm 0.006$ .

The variations in concentration of particles depend on welding parameters and environmental factors. Working procedures and general and personal prevention systems have an influence on concentrations in fumes.

Also, the presence of some other processes applied in the vicinity affects the chemical composition of the background; under certain conditions, the background may significantly affect the fumes collected in the breathing zone, although usually the background concentration of fumes measured with stationary samplers constitutes about one tenth of that found in the breathing zone.<sup>16,17</sup>

Relations exist between concentrations of elements in fumes and distance from the welding area. The results of our studies indicate that MMA/SS fumes and their elements are usually more concentrated in

the breathing zone than in the workplaces.<sup>15</sup> The individual samples may contain higher percentages of Cr and Mn compared with the stationary samples but a lower Fe percentage.<sup>17</sup>

The data published by the International Agency for Research on Cancer<sup>2</sup> show that evaluation of occupational exposure to fumes under some determined conditions can be estimated by combining information on the elemental abundance of the aerosol as determined from a chemical analysis of welding fumes produced in the laboratory under controlled conditions,<sup>18</sup> and the total aerosol concentration expected on the basis of measurements in the workplace. The disadvantage of this technique, however, is that the actual composition of specific welding fumes cannot be determined.

Although the average percentage of elements in MMA/SS welding fumes found in our study (table 3) is similar to the percentage reported by some other authors (Cr 2-9.2; Ni 0.2-3.3; Fe 3.3-15.9; Mn 1.4-14%),<sup>2,18-21</sup> mean statistical values of particular elements in the welders' breathing zone do not form a real picture of exposure.

The data presented (fig 3) indicate that different conditions at the workplace may result in variations in the chemical composition of the fumes. Therefore,

**Table 2** Mean content of the elements in MMA/SS welding fumes (plants A, B, C, D)

Elements (%)				
Fe	Mn	Cr	Ni	F
11.2 (2.1)	3.9 (0.6)	3.6 (0.5)	0.5 (0.2)	3.3 (0.6)

Confidence intervals in parentheses.

Table 3 Mean content of particular Cr compounds in MMA/SS welding fumes (plants A, B, C, D)

Cr compounds (Cr)	No of measurements	% Cr in fumes	N*	% Cr fume
Soluble Cr	44	1.7 (0.4)	28	2.3 (0.4)
Soluble Cr VI	44	1.4 (0.4)	14	2.3 (0.5)
Total Cr VI	44	1.5 (0.4)		
insoluble Cr III	60	2.5 (0.3)	35	2.9 (0.4)
Total Cr III	44	1.3 (0.4)	28	1.6 (0.6)
	44	1.6 (0.4)		
	60	1.1 (0.3)	45	2.3 (0.5)

Confidence intervals in parentheses. \*Number of measurements above detection limit

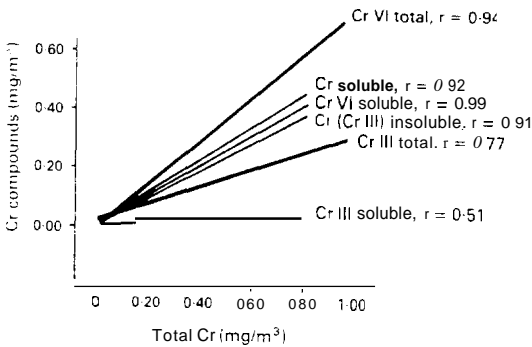


Figure 6 Relation between TWA (8 h) concentrations of particular Cr compounds and total Cr in MMA/SS welding fumes (plants A, B, C, D).  $y = kx + k$  for: total Cr VI  $0.685x \pm 0.076$ ; soluble Cr  $0.526x \pm 0.073$ ; soluble Cr VI  $0.507x \pm 0.032$ ; insoluble Cr III  $0.479x \pm 0.066$ ; total Cr III  $0.318x \pm 0.067$ ; soluble Cr III  $0.082x \pm 0.037$ .

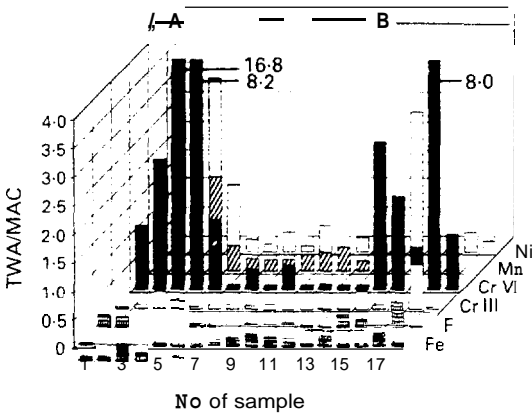


Figure 7 Occupational exposure to elements of MMA/SS welding fumes in plants A, B. TWA = time weighted average threshold limit values (Cr III  $0.5 \text{ mg/m}^3$ , Cr VI  $0.05 \text{ mg/m}^3$ ),<sup>25</sup> MAC = maximum allowable concentration (Fe  $5 \text{ mg/m}^3$ , Mn  $0.3 \text{ mg/m}^3$ , Cr VI  $0.05 \text{ mg/m}^3$ ),<sup>26</sup> (Ni  $0.05 \text{ mg/m}^3$ )

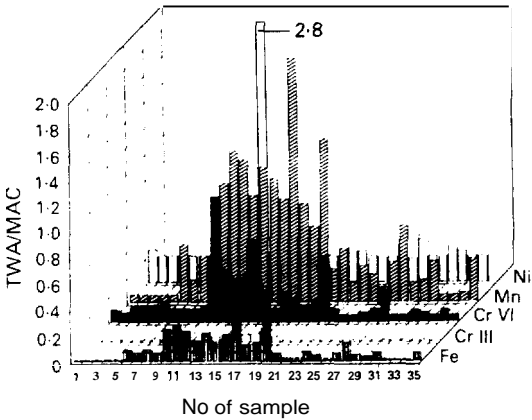


Figure 8 Occupational exposure to elements of MMA/SS welding fumes in plant C (explanation as in fig 7).

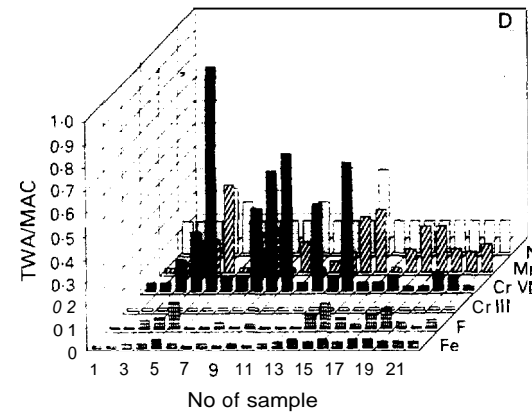


Figure 9 Occupational exposure to elements of MMA/SS welding fumes in plant D (explanation as in fig 7).

Table 4 Mean content of particular Cr compounds compared to total (plants A, B, C, D)

Cr compounds (Cr)	No of measurements	Cr %		No *	Cr %	
		Total Cr			Total Cr	
Soluble Cr	44	52.4	(5.7)	28	52.6	(7.3)
Soluble Cr III	44	8.7	(2.7)	22	8.2	(3.7)
Soluble Cr VI	44	44.7	(5.1)	14	50.7	(3.2)
Total Cr VI	44	46.2	(5.0)			
	60	68.3	(5.7)	35	68.5	(7.6)
Insoluble Cr	44	47.7	(5.5)	32	47.9	(6.6)
Insoluble Cr III	44	45.6	(5.5)	28	46.0	(6.9)
Total Cr III	44	53.9	(4.9)			
	60	31.8	(5.8)	45	31.8	(6.7)

Confidence intervals in parentheses. \*Number of measurements above detection limit.

Table 5 Occupational exposure of MMA/SS welders to particular Cr compounds

Plant	No $\geq$ TLV/No (max TWA TLV)					
	Soluble		Total	Insoluble		Total
	Cr III	Cr VI	Cr VI	Cr III	Cr VI	Cr III
A	—	3/3 (3.7)	8/8 (16.8)	—	—	—
B	—	4/13 (15.4)	4/13 (8.0)	—	1/13 (1.3)	—
C	—	1/18 (1.3)	1/18 (1.0)	—	1/18 (1.3)	—
D	—	3/10 (2.0)	1/22 (1.0)	—	—	—
A + B + C + D	—	11/44 (15.4)	14/60 (16.8)	—	2/41 (1.3)	—
TLV (mg/m <sup>3</sup> )	0.5 <sup>25</sup>	0.025 <sup>26</sup>	0.05 <sup>25</sup>	0.5 <sup>25</sup>	0.01 <sup>26,27</sup>	0.55

TLV = threshold limit value; TWA = time weighted average.

individual measurements in the breathing zone of welders during a shift are absolutely necessary to determine the risk of exposure.

In recent studies<sup>9</sup> considerable attention has been paid to the oxidation state of Cr in welding fumes, and it has always been taken into account in our previous<sup>15</sup> and current studies. In most studies on MMA/SS fumes, the concentration of Cr VI (mostly water soluble) ranged from 0.025 to 1.550 mg/m<sup>3</sup>.<sup>2,9,10,22</sup>

In our studies, the occurrence of high concentrations of Cr VI in MMA/SS fumes (range 0.005–0.8 mg/m<sup>3</sup>; fig 2) was confirmed as well as a high relative content of total Cr VI with high concentrations of soluble Cr VI (tables 2–4, figs 3–6). A considerable excess over the hygienic standards for individual exposure<sup>25–29</sup> was also noted (table 5, figs 7–9).

The high Cr VI content (36–100% of total Cr) in MMA/SS fumes is attributed to the presence of alkaline metals in the flux coating. In the study of Kobayashi and Tsutsumi,<sup>23</sup> potassium was replaced by sodium in a modified electrode, resulting in a significant reduction in the relative Cr VI content (soluble Cr VI – 5.6%, insoluble Cr VI – 11.2%). Actually, the insoluble Cr VI content in MMA/SS

welding fumes ranged from 0.03 to 0.92%<sup>2,18,21,24</sup> and CrO<sub>3</sub> content from 0.4–1.8%. The mean value of 0.2–0.3% is negligible from the point of view of exposure.<sup>7</sup>

In our study, however, we found that insoluble Cr VI content in welding fumes varied from 0.1 to 1.2%, in dust with an average 0.3%.

The data on the insoluble Cr VI content in MMA/SS welding fumes, especially in industry, have been a subject of discussion. Taking into account the fact that Cr VI has been considered to be a human carcinogen: no safe level for Cr VI can be recommended. It seems that its occurrence in fumes even at a concentration less than 0.005–0.842 mg/m<sup>3</sup> may create a serious health risk (fig 2, table 5).

#### CONCLUSIONS

Evaluation of occupational exposure has indicated that MMA/SS welders may exceed the admissible concentrations of soluble and insoluble Cr VI, Mn, and Ni.

Due to various changeable parameters in the working environment, the content of fumes in the welders' breathing zone is not constant and hence it is not possible to use one universal exposure indicator

allowing for a standard mean content of fumes. The evaluation of exposure should be based on the results of measurements of particular elements of fumes in the welders' breathing zone.

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